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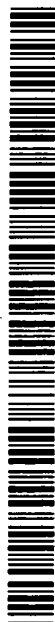
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(54) Title: COMPOSITIONS AND METHODS FOR IMPARTING IMPROVED RHEOLOGY ON PIGMENT BASED INKS AND PAINTS

(57) Abstract: Pigment compositions comprising an organic pigment and a combination of at least two normally water-soluble coloured compounds (dyes) of opposing charge, i.e. of at least one anionic and one cationic dye are provided. The compositions impart improved rheology on non-aqueous pigment based printing inks and paints.



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Compositions and methods for imparting improved rheology on pigment based inks and paints

The present invention is directed to pigment compositions containing besides an organic pigment at least two coloured compounds of opposing charge, and ink/paint compositions containing same.

The ink/paint compositions show improved rheological (flow) performance and no loss or almost no loss in colour strength.

In order to improve the flow properties of pigment compositions, it is known from GB-A-1'356'253 to incorporate in diarylide pigments (1) water-soluble azo dyestuffs which have the same general chemical structure as the pigment but contain acidic groups and (2) fatty alcohols, fatty acids, fatty esters or fatty amines.

One of the pair of agents (1) and (2) is not coloured and therefore does not contribute colour intensity to the pigment composition. In addition the non-coloured portion can interfere with the performance of other pigment additives, and lithographic properties of resulting inks can be affected leading to printing problems.

US-A-4'461'647 describes so-called fluidized agents which are water-insoluble asymmetric dyestuffs substituted by long chain ammonium salts which are added to pigment dispersions in order to enhance their fluidity and flocculation resistance.

Fluidizing agents are restricted to pigment derivatives and can suffer from colour strength loss, lithographic problems and interference with other pigment additives.

There is a need in pigment industry, therefore, to pigment compositions to be used in inks and paints with improved rheological properties (stability to flocculation) and good coloristic effects.

It has now been found surprisingly that pigment compositions comprising an organic pigment and a combination (complex) of at least two, normally water-soluble, coloured compounds (dyes) of opposing charge, e.g. of at least one anionic and one cationic dye, which dyes are readily available ones, as dispersants for the pigment, can largely overcome the mentioned problems of conventional pigment compositions.

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It is assumed that the dyes of opposing charge are complexed in such a way as to be retained within the pigment composition. Alternatively, the retention of both the dyes by separate desolubilisation mechanisms is also possible.

Accordingly, the present invention provides in a first aspect, a pigment composition comprising (1) an organic pigment and (2) a combination of at least one anionic and at least one cationic coloured compound wherein the combination (2) comprises

- (a) at least one anionic and at least one cationic dye, each of a chemical structure differing from that of the organic pigment (1),
- (b) at least one anionic and at least one cationic pigment derivative, the chemical structure of at least one of which is not derived from said organic pigment (1), or
- (c) mixtures of (a) and (b).

In a second aspect, the present invention provides said pigment composition as a solid composition, preferably as a pigment powder or as pigment granules.

In a further aspect, the present invention provides a non-aqueous composition, preferably a non-aqueous pigment dispersion.

In another aspect, the present invention provides methods for preparing said solid or non-aqueous pigment compositions.

In yet another aspect, the present invention provides non-aqueous inks or paints (oil ink or paint compositions, based e.g. on petroleum distillates) containing said pigment dispersions, and methods for preparing them.

In yet another aspect, the present invention provides the use of said non-aqueous inks or paints (ink or paint compositions) in printing and paint systems.

These and further aspects of the present invention will be described in the following.

The basis for the inventive pigment composition can be from the range of organic pigments such as, but not exclusively, monoazo, disazo, naphthol, dioxazone, azomethine, azocondensation, metal complex, nitro, perinone, quinoline, anthraquinone,

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benzimidazolone, isoindoline, isoindolinone, quinacridone, hydroxyanthraquinone, aminoanthraquinone, anthrapyrimidine, indanthrone, flavanthrone, pyranthrone, anthantrone, isoviolanthrone, diketopyrrolopyrrole, carbazole, perylene, indigo or thioindigo pigments.

The range of interesting organic pigments may comprise monoazo, disazo, naphthol, dioxazone, azomethin, azocondensation, metal complex, nitro, perinone, quinoline, anthraquinone, benzimidazolone, isoindoline, isoindolinone, quinacridone, hydroxyanthraquinone, aminoanthraquinone, anthrapyrimidine, indanthrone, flavanthrone, pyranthrone, anthantrone, isoviolanthrone, diketopyrrolopyrrole, carbazole, indigo or thioindigo pigments.

Mixtures of the pigments may be used.

Examples of these pigments and also further pigments can be found in the monograph: W. Herbst, K. Hunger "Industrielle Organische Pigmente," 2<sup>nd</sup> edition, 1995, VCH Verlagsgesellschaft.

Preferred pigments for the application of the present invention are mono- or disazo pigments, preferably mono- or diarylides, or metal complexes, preferably a copper phthalocyanine pigment, or naphthol pigments, preferably  $\beta$ -naphthol or a  $\beta$ -oxynaphthoic acid (BONA) pigments, or quinacridones or indanthrones.

More preferably, the following organic pigments are used inventively:

Mono- or diarylide yellow pigments selected from C.I. Pigment Yellow 1, 2, 10, 12, 13, 14, 17, 61, 62, 63, 64, 65, 73, 74, 75, 83, 127, 168, 174, 176, 188 and 191.

Monoarylide yellow pigments selected from C.I. Pigment Yellow 1, C.I. Pigment Yellow 2, C.I. Pigment Yellow 65, C.I. Pigment Yellow 73, C.I. Pigment Yellow 74 and C.I. Yellow 75.

Diarylide yellow pigments selected from C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 17 and C.I. Pigment Yellow 83.

Disazo orange pigments selected from C.I. Pigment Orange 16 and C.I. Pigment Orange 34.

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Naphthol red pigments selected from C.I. Pigment Red 48:1, C.I. Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 48:4, C.I. Pigment Red 48:5, C.I. Pigment Red 49:1, C.I. Pigment Red 52:1, C.I. Pigment Red 52:2, C.I. Pigment Red 52:3, C.I. Pigment Red 53:1, C.I. Pigment Red 53:2, C.I. Pigment Red 53:3, C.I. Pigment Red 57:1, C.I. Pigment Red 57:2, C.I. Pigment Red 58:2, C.I. Pigment Red 58:4, C.I. Pigment Red 63:1 and C.I. Pigment Red 64:1.

Quinacridone red pigments such as C.I. Pigment Red 202.

Blue or green copper phthalocyanine pigments selected from C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:2, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Green 7 and C.I. Pigment Green 36.

Blue indanthrone pigments such as C.I. Pigment Blue 60.

The anionic dyes are typically, but not exclusively, commercially available dyes selected from acid dyes, direct dyes, reactive dyes and mordant dyes. As a rule, their chemical structure is different from that of the organic pigment.

Preferred are the following anionic dyes to be used inventively:

Acid dyes selected from C.I. Acid Black 1, 24 and 48, C.I. Acid Blue 1, 7, 9, 25, 29, 40, 45, 74, 80, 83, 90, 92, 113, 120, 129 and 147, C.I. Acid Green 1, 3, 5, 25, 27, and 50, C.I. Acid Orange 6, 7, 8, 10, 12, 51, 52, 63 and 74, C.I. Acid Red 1, 4, 8, 14, 17, 18, 26, 27, 29, 37, 44, 50, 51, 52, 66, 73, 88, 97, 103, 114, 150, 151 and 183, C.I. Acid Violet 7 and 17, and C.I. Acid Yellow 1, 9, 11, 17, 23, 25, 29, 34, 36, 42, 54, 76, 99 and 169.

Direct dyes selected from C.I. Direct Blue 1, 14, 53 and 71, C.I. Direct Violet 51, C.I. Direct Red 2, 23, 28, 75, 80 and 81, and C.I. Direct Yellow 4, 8, 9, 12, 27, 50, 62 and 172.

Reactive dyes selected from C.I. Reactive Black 5, C.I. Reactive Blue 2, 4 and 15, C.I. Reactive Orange 16, C.I. Reactive Red 2 and 4, and C.I. Reactive Yellow 2.

Mordant dyes selected from C.I. Mordant Black 17 and C.I. Mordant Violet 5.

One or more anionic dyes can be used in the inventive pigment compositions.

The anionic dyes may also be pigment derivatives bearing one or more anionic, i.e. acidic groups which impart to them a (certain) water solubility. Examples of such groups are inorganic groups derived from mineral acids comprising sulfonic acid, sulfonate, sulfinic acid, sulfinate, phosphoric acid, phosphate groups, and organic groups derived from carboxylic acids/carboxylates (carboxylic acid salts).

The anionic pigment derivative may be a derivative of organic pigment (1), on the one hand, but also need not to be of similar structure to organic pigment (1), on the other hand.

As a rule, the anionic pigment derivatives give good results when associated with a non-derivative cationic dye.

Preferred anionic pigment derivatives are those derived from the preferred pigments mentioned hereinbefore.

The cationic dyes are typically, but not exclusively, also commercially available dyes which may be - according to their chemical characterization - azo, azomethine, methine, polymethine, azine, cyanine, oxazine, thiazine, thiazole, acridine, anthraquinone, triarylmethane, xanthene or ketone imine dyes. Their chemical structure is generally different from that of pigment (1).

Preferred are the following cationic dyes to be used inventively:

Cationic black dyes selected from C.I. Basic Black 2 and C.I. Basic Black 7.

Cationic blue dyes selected from C.I. Basic Blue 1, 3, 6, 7, 9, 11, 12, 16, 17, 24, 26, 40, 41, 57, 66, 80, 123 and 159.

Cationic green dyes selected from C.I. Basic Green 1, 4 and 5.

Cationic orange dyes selected from C.I. Basic Orange 2, 14, 21 and 54.

Cationic red dyes selected from C.I. Basic Red 1, 2, 5, 9, 10, 13, 22, 29, 46 and 54.

Cationic violet dyes selected from C.I. Basic Violet 1, 2, 3, 4, 10 and 35.

Cationic yellow dyes selected from C.I. Basic Yellow 1, 2, 11, 13, 17, 19, 21, 24, 28, 40, 45, 53, 61, 63 and 73.

One or more cationic dyes can be used in the inventive pigment compositions.

The cationic dye may also be a pigment derivative bearing one or more basic (basic means cationic) groups which impart to them a (certain) water solubility. Typical examples of cationic groups include ammonium groups ( $-NH_4$ ) which may be primary, secondary, tertiary or quaternary substituted, further primary, secondary or tertiary amino groups, and also primary, secondary and tertiary carbon amido, sulfonamido, sulfinamido or phosphoramido.

The cationic pigment derivative may be a derivative of organic pigment (1), on the one hand, but also need not to be of similar structure to organic pigment (1), on the other hand. Preferred cationic pigment derivatives are those derived from the preferred pigments mentioned hereinbefore.

The cationic pigment derivatives can be combined with non-derivative anionic dyes to give good results, too.

When a combination of an anionic and a cationic pigment derivative is used in the inventive pigment compositions, one of said pigment derivatives is not derived from organic pigment (1), i.e. this derivative has to show a different chemical structure from the base structure of organic pigment (1).

When using alternative (2c) – covering mixtures of (2a) and (2b) – the general proviso that the compounds used must be anionic and cationic should be always observed.

Combination (2) of the inventive pigment compositions preferably comprises such pairs as: (anionic=negatively charged; cationic=positively charged)

cationic dye + anionic dye (2a),

cationic pigment derivative + anionic dye (2c),

cationic dye + anionic pigment derivative (2c), or

cationic pigment derivative + anionic pigment derivative (2b)

(the two pigment derivatives must be structurally different)

Alternatively, it has been found that at least a partial replacement of the anionic/cationic coloured compound (anionic/cationic dye or anionic/cationic pigment derivative) with an anionic/cationic surfactant, respectively, can also lead to inventive pigment compositions with

sufficient performance. As a rule, up to about 3/4 (0 to 75 mol%) of the anionic/cationic dye (anionic/cationic pigment derivative) can be replaced by an anionic/cationic surfactant, respectively. As a preferred range for this replacement 0 to 50 mol% can be considered.

Suitable surfactants are known to those skilled in the art. Preferably they comprise e.g. long chain (fatty, containing e.g. 8 to 22, preferably 8 to 18 carbon atoms) alcohols, acids, esters, amides or amines and their derivatives, such as alkoxylates (ethoxylates), which contain positively/negatively charged groups.

In this context, reference is made to the relevant textbooks, scientific or technical publications.

Preferred combinations (2) – when anionic/cationic surfactants are used – comprise:

cationic dye/cationic surfactant + anionic dye,  
cationic dye/cationic surfactant + anionic pigment derivative,  
cationic pigment derivative/ cationic surfactant + anionic dye,  
cationic pigment derivative/ cationic surfactant + anionic pigment derivative (the two pigment derivatives must be structurally different), or  
anionic pigment derivative/anionic surfactant + cationic pigment derivative (the two pigment derivatives must be structurally different), and also  
anionic dye/anionic surfactant + cationic dye,  
anionic dye/anionic surfactant + cationic pigment derivative ,or  
anionic pigment derivative/anionic surfactant + cationic dye

The molar ratio of the components – assuming that both are mono-anionic and monocationic - of combination (mixture) (2a)(anionic and cationic dye), (2b) (anionic and cationic pigment derivative), or (2c) can vary within a broad range. Possible ratios of about (0.1-10) : (10-0.1), or more preferred of (1-5) : (5-1) can be used.

C.I. means Colour Index as compiled by the by The Society of Dyers and Colourists and The American Association of Textile Chemists and Colourists.

Details, such as descriptions and definitions, for the mentioned pigments, the anionic dyes as acid, direct, reactive and mordant dyes, and the cationic (basic) dyes can be found there.



The inventive compositions of organic pigments or organic pigment compositions (the latter may include typical additives such as abietyl resins, other rheology modifiers and ink vehicle components) may contain usually from 50.1 to 99.8% by weight (b.w.), preferably from 80.0 to 99.0% (b.w.) of the pigment, usually from 0.1 to 49.8% (b.w.), preferably from 0.5 to 10.0% (b.w.) of at least one anionic coloured compound (dye), and usually from 0.1 to 49.8% (b.w.), preferably from 0.5 to 10% (b.w.) of at least one cationic coloured compound (dye). Preferably the combined amount of anionic/cationic coloured compounds in the pigment compositions is from 1 to 10% (b.w.).

Aqueous preparations of these compositions have a solids content usually from about 0.5% to 20%, preferably from 5 to 18%. Aqueous based organic pigment dispersions can be prepared from dry pigments, by use of additional surfactants, at a level of at least 50% pigment by conventional techniques.

In non-aqueous lithographic inks, pigment concentration normally is 8 to 20%. Ink concentrates, where rheology modifiers can be particularly useful, can contain up to 50% (0.5 to 50%) pigment. In certain circumstances, low pigment concentration below about 5% is also possible.

The (non-aqueous) pigment compositions may optionally contain further additives such as, but not exclusively, e.g. abietyl resins and abietyl derivatives, surfactants, pigment derivatives, extenders, ink vehicle components, rheology modifiers, etc.

Effective amounts should be used, e.g. from 0 to 50% (b.w.), based on the combined weight of the pigment and the dyes.

The dyes may be used as a solution or dispersion in water or other suitable solvent.

The dyes may also be used in press-cake, granule or dry powder form.

The dye mixture (complex of anionic and cationic dye(s)) may also deliberately be formed and isolated prior to use and utilised as a solution or dispersion in water or other suitable solvent.

The dye mixture can be isolated as a filter (press) cake, redispersed into or for use in an aqueous pigment slurry, or mixed as filter cake with a filter cake of the pigment.

The dye (mixture) complex may also be used in granule or dry powder form.

The isolated and dried material (dye mixture) can then be added to an aqueous or solvent based slurry of the pigment or blended with a dry pigment.

The anionic/cationic coloured compound (dye) may be incorporated independently or together into a preparation of pigment (1), preferably a water-based composition (dispersion), during or after its preparation by standard stirring/milling techniques (conditioning) or surface treating (coating)

Alternatively the dyes or dye complexes may be incorporated into the pigment during its synthesis, i.e. before or after coupling, but more preferably after completion of coupling, but before isolation, washing or drying.

When preparing inventive pigment compositions in solid form, such as pigment powders or pigment granules, the method comprises e.g. heating an aqueous pigment slurry (as obtained by normal synthesis steps) containing the necessary additives, to induce flocculation, followed by optional cooling and isolation which comprises such steps as filtering and washing until salt free, and then drying and/or granulating the composition. Alternatively, the method can be started by a dispersion step for the pigment in an aqueous solution of the dyestuffs (at least one anionic and at least one cationic dye).

Still another alternative comprises the co-flushing or co-drying of the pigment and the dye mixture. The preparation of flushed (pigment) compositions involves the addition of a flushing vehicle, such as an oil or a solution of resins and other additives, to the water-precipitated filter (press) cake or dispersion (slurry) of the pigment/dye mixture composition. The direct transfer (flushing) of the pigment/dye mixture from the aqueous phase to the oil or non-polar phase is effected by kneading the filter cake and the vehicle together in a flusher or heavy-duty mixer under heat and vacuum.

The dye mixture (complex) can also be used in surface treated (coated) form, i.e. treated e.g. with abietyl resins or fatty acids, in any one of the methods described before

The inventive pigment compositions may be used in all customary industrial printing processes such as lithographic, flexographic, gravure, letterpress, screen, ink-jet, intaglio, aqueous or other printing inks, further in all customary industrial paint systems such as decorative, industrial, automotive or other paint systems, to provide improved rheology with no or at most minimalized reduction of colour strength.

The method of preparation of the ink system is by methods of shear to induce dispersion into a varnish system. Examples of the wide range of techniques are triple-roll-mill and bead mill. Varnish systems are also wide ranging and known by the artisan.

Examples of the final application are off-set lithography and sheet fed.

Alternatively, when preparing the printing inks or paint systems, the dyes may be incorporated independently or together (dye complexes) to a conventional ink or paint formulation before, during or after pigment addition.

For the preparation of the inks and paints corresponding high molecular weight organic substances, such as binders, synthetic resin dispersions etc. and the inventive pigment compositions are usually dispersed or dissolved together, optionally together with customary additives, such as dispersants, fillers, paint auxiliaries, siccatives, plasticizers and/or additional pigments or pigment precursors, in a common solvent or mixture of solvents. This can be achieved by dispersing or dissolving the individual components by themselves, or also several components together, and only then bringing all components together, or by adding everything together simultaneously.

It is the use of at least two dyes of opposing charge (dye complex) as part of a pigment composition which gives the inventive pigment compositions their particularly useful properties and advantageous effects, i.e. their improved rheological (flow) performance combined with no or at most a minimum loss in colour strength, over pigment compositions of the state of the art.

The desired effects and the other by-properties can be moderated by the appropriate selection of the relative ratio and total amount of the two dyes. The dyes should also be selected that undesirable effects on product shade do not occur. As the pair of materials (dye complex) which are responsible for the improved rheological performance are both coloured, in general of the the same colour, almost no loss in colour strength is observed.

The present invention is further illustrated by, but not restricted to, the following examples in which all parts and percentages are by weight unless otherwise indicated. The temperatures are given in degrees centigrade.

## Examples:

### Example 1

To a stirred C.I. Pigment Yellow 13 aqueous slurry containing 63 g of the pigment, an aqueous solution containing 2 g of 4,4'-bis[[1-[(2,4-dimethylphenyl)amino]carbonyl]-2-oxypropyl]azo]-[1,1'-biphenyl]-2,2'-disulphonic acid is added, followed by an aqueous solution containing 3.5 g of C.I. Basic Yellow 40. Following this an aqueous solution of Burez K50-505A potassium salt (potassium soap of disproportionated rosin, 50%, Eka-Nobel), containing the equivalent of 30 g resin acids, is added and the resulting slurry heated to roughly 95°C by direct steam injection.

The slurry is acidified by dropwise addition of dilute hydrochloric acid, then cooled, filtered and washed until salt free. The product presscake is dried giving 94 g (= 95% yield).

The resulting dye pair is thus formed in situ during pigment processing.

### Example 2

The Example 1 procedure is repeated with 64 g of C.I. Pigment Yellow 13 plus 2.5 g of C.I. Basic Yellow 28 in place of C.I. Basic Yellow 40.

### Example 3

The Example 1 procedure is repeated with 63.8 g of C.I. Pigment Yellow 13 plus 1.7 g of C.I. Basic Yellow 17 in place of C.I. Basic Yellow 40.

### Example 4

The Example 1 procedure is repeated with 64.1 g of C.I. Pigment Yellow 13 plus 2.4 g of C.I. Basic Yellow 13 in place of C.I. Basic Yellow 40.

### Example 5

The Example 1 procedure is repeated with 64 g of C.I. Pigment Yellow 13 plus 2.5 g of C.I. Basic Yellow 45 in place of C.I. Basic Yellow 40.

#### Comparative Examples A to D:

##### Example A

The Example 1 procedure is repeated with 66.5 g of C.I. Pigment Yellow 13 and no added C.I. Basic Yellow 40.

##### Example B

The Example 1 procedure is repeated with 68.5 g of C.I. Pigment Yellow 13 and no additions of either C.I. Basic Yellow 40 or 4,4'-bis[[1-[(2,4-dimethylphenyl)amino]carbonyl]-2-oxypropyl]azo]-[1,1'-biphenyl]-2,2'-disulphonic acid.

##### Example C

The Example 1 procedure is repeated with 65 g of C.I. Pigment 13 but in absence of 4,4'-bis[[1-[(2,4-dimethylphenyl)amino]carbonyl]-2-oxypropyl]azo]-[1,1'-biphenyl]-2,2'-disulphonic acid.

##### Example D

The Example 1 procedure is repeated with 66 g of C.I. Pigment 13 but in absence of 4,4'-bis[[1-[(2,4-dimethylphenyl)amino]carbonyl]-2-oxypropyl]azo]-[1,1'-biphenyl]-2,2'-disulphonic acid. 2.5 g of C.I. Basic Yellow is also used in place of C.I. Basic Yellow 45.

##### Example 6

A stirred aqueous slurry containing C.I. Pigment Blue 15:3 ( $\beta$ -copper phthalocyanine) is heated to 90°C. A slurry containing 2.5 g of copper phthalocyanine monosulfonic acid is added and stirring continued for 30 minutes. An aqueous solution containing the equivalent of 4 g of C.I. Basic Blue 9 (Methylene Blue) is then added and stirring continued for 30 minutes more. The resulting slurry is cooled, filtered and washed until salt free, then dried giving 58 g of pigment composition.

##### Example 7

To a stirred aqueous slurry of 6.1 g of copper phthalocyanine monosulfonic acid at pH of 11 is added 3.49 g of C.I. Basic Blue 9. An aqueous solution containing 3.25 g of dodecylbenzene-p-sulfonic acid, sodium salt, is added and then the resulting slurry is filtered and dried, giving a yield of 9.58 g (78%).

This dry complex is added at a 3% level to a stirred aqueous slurry of C.I. Pigment Blue 15:3 at 30°C and pH 1. After stirring for 1 hour the slurry is filtered, washed until salt free and dried.

Instead of the sodium salt of dodecylbenzene-p-sulfonic acid an appropriate amount of a long chain alkyl (C<sub>12</sub>-C<sub>18</sub>) quaternary ammonium chloride can be used giving likewise good results.

#### Example 8

To a stirred aqueous slurry of 12.12 g of copper phthalocyanine monosulfonic acid at pH of 11 is added 3.74 g of C.I. Basic Blue 9 and the resulting slurry is filtered and dried giving a yield of 11.84 g (74%).

This dry complex is added at a 3% level to a stirred aqueous slurry of C.I. Pigment Blue 15:3 at 30°C and pH 1. After stirring for 1 hour the slurry is filtered, washed until salt free and dried.

#### Comparative Examples E to G:

##### Example E

The Example 6 procedure is repeated in the absence of C.I. Basic Blue 9.

##### Example F

The Example 6 procedure is repeated in the absence of both C.I. Basic Blue 9 and copper phthalocyanine monosulfonic acid.

##### Example G

The Example 8 procedure is repeated in the absence of both C.I. Basic Blue 9 and copper phthalocyanine monosulfonic acid.

#### Test Method:

The products of the foregoing examples were used to prepare aqueous dispersions containing 20% pigmentation which are tested into a commercial heatset varnish system on a Buhler SDY-200 three roll mill.

The inks are then reduced to between 12 to 16% pigmentation (depending on the pigment type) by the addition of further varnish.

Colouristic assessment is carried out on the prints produced from a Prufbau Printer and low shear flow assessed on a 45° angled plate after 2 or 24 hours, depending on the the pigment type (2 hours for yellow and red pigment compositions, 24 hours for blue pigment compositions).

The figures in Table 1 are quoted in comparison to a commercial pigment standard (low shear flow and colour strength – 100%, each).

Table 1:

Example No,	Low Shear Flow [%]	Colour Strength [%]
1	195	100
2	150	110
3	140	100
4	130	100
5	140	100
A (Comparison)	95	105
B (Comparison)	90	110
C (Comparison)	90	110
D (Comparison)	110	95
6	290	100
7	220	100
8	160	100
E (Comparison)	170	100
F (Comparison)	100	100
G (Comparison)	100	100

#### Example 9

This example relates to an isolated complex of a dyestuff pair as an ink additive.

An 80ml aqueous solution containing 2.0g 4,4'-bis[[1-[[[(2,4-dimethylphenyl)amino]carbonyl]-2-oxypropyl]azo]-[1,1'-biphenyl]-2,2'-disulphonic acid is mixed thoroughly with an 80ml aqueous solution containing the equivalent of 1.5g cation weight of Basic Yellow 28. To this mixture a 45ml aqueous solution of Burez K50-505A potassium salt, containing the

equivalent of 1.6g resin acids, is added resulting in increased alkalinity (pH 9.5). The mixture is heated to 60°C and the pH reduced to 5.0 by the addition of dilute hydrochloric acid. The resulting material was filtered, washed and dried giving a 90% yield. The dry product is ground and blended with a standard diarylide yellow composition (Pigment Yellow 174) at a weight ratio of 1:19 respectively.

Table 2:

	Low shear flow	Strength
Example 9	240%	102%
Comparative Example H (Pigment Yellow 174 alone)	100%	100%

#### EXAMPLE 10

To a stirred aqueous slurry containing 13.12 g of copper phthalocyanine monosulfonic acid at pH 11 is added 3.74 g of C.I. Basic Blue 9. The pH is returned to 11 and the resulting slurry filtered. The product is held as a press-cake.

The equivalent of 1.5 g dry weight is re-dispersed into a stirred aqueous based slurry containing 50 g pigmentary C.I. Pigment Blue 60 and the resulting mixture heated to 70°C. After stirring for 50 minutes the slurry is filtered, washed until salt free and dried.

#### EXAMPLE 11

To a stirred aqueous slurry containing 13.12 g of copper phthalocyanine monosulfonic acid at pH 11 is added 3.74 g of C.I. Basic Blue 9. The pH is adjusted to 2 and the resulting slurry filtered. The product is held as a filter cake.

The equivalent of 1.5g dry weight of the filter cake is re-dispersed into a stirred aqueous based slurry containing 50g pigmentary C.I. Pigment Blue 60 and the resulting mixture heated to 70°C. After stirring for 50 minutes the slurry is filtered, washed until salt free and dried.



**EXAMPLE J**

A stirred aqueous based slurry containing 50 g pigmentary C.I. Pigment Blue 60 is heated to 70°C. After stirring for 50 minutes the slurry is filtered, washed until salt free and dried.

This material is used as a standard for comparison with examples 10 and 11.

Table 3:

Example No.	Low Shear Flow [%]	Colour Strength [%]
10	>140%	100%
11	>140%	100%
J (Comparison)	100%	100%

**EXAMPLE 12**

To a stirred aqueous based slurry containing 7.84 g quinacridone monosulfonic acid at pH 11 is added 3.56 g Basic Red 46. The pH is returned to 11 and the slurry filtered. The product is held as a filter cake.

The equivalent of 1.2 g dry weight of the filter cake is re-dispersed into a stirred aqueous based slurry containing 40 g of crystalline pigmentary Pigment Red 202. The slurry is then heated to 70°C and held for 30 minutes then filtered, washed salt free and dried.

**EXAMPLE 13**

To a stirred aqueous based slurry containing 3.5 g quinacridone monosulphonic acid at pH 3 is added 3.67 g Basic Red 46. The pH is then taken to 11 and an aqueous solution of Burez K50-505A containing the equivalent of 1.5 g resin acids is added. The pH is then slowly reduced to 5.0 by dilute hydrochloric acid addition and the product filtered, washed salt free and dried.

1 g of this dry material is blended with 30 g dry crystalline pigmentary Pigment Red 202.

**EXAMPLE 14**

To a stirred aqueous based slurry containing 3.5 g quinacridone monosulphonic acid at pH 7 is added an aqueous solution containing 3.67 g Basic Red 46 at pH7. The mixture is stirred for 50 minutes then filtered, given a mild wash and dried.

1.2 g of the dry material is combined with 40g size-reduced crude Pigment Red 202 in a traditional solvent conditioning treatment. The slurry is then allowed to cool, filtered, washed thoroughly and dried.

#### EXAMPLE K

120 g crystalline pigmentary Pigment Red 202 is prepared from size-reduced crude Pigment Red 202 in a traditional solvent conditioning treatment. The slurry is then isolated as a filter cake and washed thoroughly. This material is used as crystalline pigmentary Pigment Red 202 in examples 12 and 13. A portion is also dried and used as a comparative standard for examples 12, 13 and 14.

Table 4:

Example No.	Low Shear Flow [%]	Colour Strength [%]
12	320	100
13	145	100
14	340	105
K (Comparison)	100	100

## Claims:

1. A pigment composition comprising (1) an organic pigment and (2) a combination of at least one anionic and at least one cationic coloured compound wherein the combination (2) comprises
  - (a) at least one anionic and at least one cationic dye, each of a chemical structure differing from that of the organic pigment (1),
  - (b) at least one anionic and at least one cationic pigment derivative, the chemical structure of at least one of which is not derived from said organic pigment (1), or
  - (c) mixtures of (a) and (b).
2. The pigment composition according to claim 1 wherein the organic pigment is a monoazo, disazo, naphthol, dioxazone, azomethin, azocondensation, metal complex, nitro, perinone, quinoline, anthraquinone, benzimidazolone, isoindoline, isoindolinone, quinacridone, hydroxyanthraquinone, aminoanthraquinone, anthrapyrimidine, indanthrone, flavanthrone, pyranthrone, anthanthrone, isoviolanthrone, diketopyrrolopyrrole, carbazole, perylene, indigo or thioindigo pigment.
3. The pigment composition according to claim 2 wherein the organic pigment is a mono- or disazo pigment, preferably a mono- or diarylide, a metal complex, preferably a copper phthalocyanine pigment, an indanthrone or a quinacridone.
4. The pigment composition according to claim 2 wherein the organic pigment is a mono- or disazo pigment, preferably a mono- or diarylide, or a metal complex, preferably a copper phthalocyanine pigment.
5. A pigment composition according to claim 2 wherein the organic pigment is a naphthol pigment, preferably a  $\beta$ -naphthol or a  $\beta$ -oxynaphthoic acid (BONA) pigment.
6. The pigment composition according to claim 4 wherein the organic pigment is a mono- or diarylide yellow pigment selected from C.I. Pigment Yellow 1, 2, 10, 12, 13, 14, 17, 61, 62, 63, 64, 65, 73, 74, 75, 83, 127, 168, 174, 176, 188 and 191.

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7. The pigment composition according to claim 4 wherein the organic pigment is a disazo orange pigment selected from C.I. Pigment Orange 16 and C.I. Pigment Orange 34.

8. The pigment composition according to claim 3 wherein the organic pigment is a naphthol red pigment selected from C.I. Pigment Red 48:1, C.I. Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 48:4, C.I. Pigment Red 48:5, C.I. Pigment Red 49:1, C.I. Pigment Red 52:1, C.I. Pigment Red 52:2, C.I. Pigment Red 52:3, C.I. Pigment Red 53:1, C.I. Pigment Red 53:2, C.I. Pigment Red 53:3, C.I. Pigment Red 57:1, C.I. Pigment Red 57:2, C.I. Pigment Red 58:2, C.I. Pigment Red 58:4, C.I. Pigment Red 63:1 and C.I. Pigment Red 64:1, or a quinacridone red pigment being C.I. Pigment Red 202.

9. The pigment composition according to claim 5 wherein the organic pigment is a naphthol red pigment selected from C.I. Pigment Red 48:1, C.I. Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 48:4, C.I. Pigment Red 48:5, C.I. Pigment Red 49:1, C.I. Pigment Red 52:1, C.I. Pigment Red 52:2, C.I. Pigment Red 52:3, C.I. Pigment Red 53:1, C.I. Pigment Red 53:2, C.I. Pigment Red 53:3, C.I. Pigment Red 57:1, C.I. Pigment Red 57:2, C.I. Pigment Red 58:2, C.I. Pigment Red 58:4, C.I. Pigment Red 63:1 and C.I. Pigment Red 64:1.

10. The pigment composition according to claim 3 wherein the organic pigment is a blue or green copper phthalocyanine pigment selected from C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:2, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Green 7 and C.I. Pigment Green 36, or an indanthrone blue pigment being C.I. Pigment Blue 60.

11. The pigment composition according to claim 4 wherein the organic pigment is a blue or green copper phthalocyanine pigment selected from C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Green 7 and C.I. Pigment Green 36.

12. The pigment composition according to claim 1 wherein the anionic dye is selected from acid dyes, direct dyes, reactive dyes and mordant dyes.

13. The pigment composition according to claim 1 wherein the anionic dye is an organic pigment derivative containing one or more acidic groups.

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14. The pigment composition according to claim 12 wherein the anionic dye is an acid dye selected from C.I. Acid Black 1, 24 and 48, C.I. Acid Blue 1, 7, 9, 25, 29, 40, 45, 74, 80, 83, 90, 92, 113, 120, 129 and 147, C.I. Acid Green 1, 3, 5, 25, 27, and 50, C.I. Acid Orange 6, 7, 8, 10, 12, 51, 52, 63 and 74, C.I. Acid Red 1, 4, 8, 14, 17, 18, 26, 27, 29, 37, 44, 50, 51, 52, 66, 73, 88, 97, 103, 114, 150, 151 and 183, C.I. Acid Violet 7 and 17, and C.I. Acid Yellow 1, 9, 11, 17, 23, 25, 29, 34, 36, 42, 54, 76, 99 and 169.

15. The pigment composition according to claim 12 wherein the anionic dye is a direct dye selected from C.I. Direct Blue 1, 14, 53 and 71, C.I. Direct Violet 51, C.I. Direct Red 2, 23, 28, 75, 80 and 81, and C.I. Direct Yellow 4, 8, 9, 12, 27, 50, 62 and 172.

16. The pigment composition according to claim 12 wherein the anionic dye is a reactive dye selected from C.I. Reactive Black 5, C.I. Reactive Blue 2, 4 and 15, C.I. Reactive Orange 16, C.I. Reactive Red 2 and 4, and C.I. Reactive Yellow 2.

17. The pigment composition according to claim 12 wherein the anionic dye is a mordant dye selected from C.I. Mordant Black 17 and C.I. Mordant Violet 5.

18. The pigment composition according to claim 1 wherein the cationic dye is an azo, azomethine, methine, polymethine, azine, cyanine, oxazine, thiazine, thiazole, acridine, anthraquinone, triarylmethane, xanthene or ketone imine dye.

19. The pigment composition according to claim 1 wherein the cationic dye is an organic pigment derivative containing one or more basic groups.

20. The pigment composition according to claim 18 wherein the cationic dye is a black dye selected from C.I. Basic Black 2 and C.I. Basic Black 7, a blue dye selected from C.I. Basic Blue 1, 3, 6, 7, 9, 11, 12, 16, 17, 24, 26, 40, 41, 57, 66, 80, 123 and 159, a green dye selected from C.I. Basic Green 1, 4 and 5, an orange dye selected from C.I. Basic Orange 2, 14, 21 and 54, a red dye selected from C.I. Basic Red 1, 2, 5, 9, 10, 13, 22, 29, 46 and 54, a violet dye selected from C.I. Basic Violet 1, 2, 3, 4, 10 and 35, or

a yellow dye selected from C.I. Basic Yellow 1, 2, 11, 13, 17, 19, 21, 24, 28, 40, 45, 53, 61, 63 and 73.

21. The pigment composition according to claim 1 wherein combination (2b) comprises an anionic pigment derivative and a cationic pigment derivative, one of said derivatives being not derived from organic pigment (1).

22. The pigment composition according to claim 1 wherein combination (2) comprises the pairs of

cationic dye + anionic dye (2a),

cationic pigment derivative + anionic dye (2c),

cationic dye + anionic pigment derivative (2c), or

cationic pigment derivative + anionic pigment derivative (2b) (the two pigment derivatives must be structurally different).

23. The pigment composition according to claim 1 comprising a partial replacement of the anionic and cationic coloured compounds with anionic and cationic surfactants, respectively.

24. The pigment composition according to claim 25 wherein combination (2) comprises the components of

cationic dye/cationic surfactant + anionic dye,

anionic dye/anionic surfactant + cationic dye,

cationic dye/cationic surfactant + anionic pigment derivative,

anionic dye/anionic surfactant + cationic pigment derivative,

cationic pigment derivative/ cationic surfactant + anionic dye,

anionic pigment derivative/ anionic surfactant + cationic dye,

cationic pigment derivative/ cationic surfactant + anionic pigment derivative (the two pigment derivatives must be structurally different), or

anionic pigment derivative/anionic surfactant + cationic pigment derivative (the two pigment derivatives must be structurally different).

25. The pigment composition according to claim 1 comprising from 50.1 to 99.8% by weight (b.w.), preferably from 80.0 to 99.0% (b.w.) of the organic pigment (1), from 0.1 to 49.8% (b.w.), preferably from 0.5 to 10.0% (b.w.) of at least one anionic coloured compound, and

from 0.1 to 49.8% (b.w.), preferably from 0.5 to 10% (b.w.) of at least one cationic coloured compound.

26. The pigment composition according to claim 27 containing further additives.

27. The pigment composition according to any one of claims 1 to 26 which is a liquid (aqueous) composition, preferably a pigment dispersion, of organic pigment (1) and said anionic and cationic coloured compounds.

28. The pigment composition according to any one of claims 1 to 26 which is a solid composition, preferably a pigment powder or pigment granules, of organic pigment (1) and said anionic and cationic coloured compounds.

29. Method for preparing the liquid (aqueous) pigment composition according to claim 27 comprising

adding said anionic and cationic coloured compounds to the organic pigment (1) during its synthesis, conditioning or surface treatment, or

adding said anionic and cationic coloured compounds separately, as aqueous composition or in dry form, to the organic pigment (1) which is in form of a slurry, or

adding a separately prepared and isolated complex of said anionic and cationic coloured compounds to the organic pigment (1) which is in form of an aqueous slurry or organic solvent preparation.

30. Method according to claim 29 wherein the separately prepared and isolated complex of said anionic and cationic coloured compounds is in the form of a presscake which is redispersed and added to the organic pigment (1) which is in form of a slurry.

31. Method for preparing the solid pigment composition according to claim 28 comprising dispersing either the organic pigment (1) in aqueous solutions of said anionic and cationic coloured compounds, or dispersing said anionic and cationic coloured compounds in dispersions (slurries) of organic pigment (1), optionally cooling the dispersions, filtering and washing them until salt free, and then drying and/or granulating the obtained presscakes.

32. Method for preparing the solid pigment composition according to claim 28 comprising co-flushing or co-drying a filter cake or dispersion (slurry) of organic pigment (1) and a filter cake or dispersion (slurry) of the separately prepared and isolated complex of said anionic and cationic coloured compounds.

33. Method of preparing the solid pigment composition according to claim 28 comprising mixing the dry organic pigment (1) with the dry complex of said anionic and cationic coloured compounds.

34. Method of preparing the liquid (aqueous) or solid pigment compositions according to any one of claims 29 to 33 wherein the said anionic and cationic coloured compounds and their complexes are surface treated (coated).

35. A non-aqueous printing ink composition or paint system comprising the pigment composition according to claim 1.

36. A method for preparing a non-aqueous printing ink composition or paint system according to claim 35 comprising adding said pigment compositions to a conventional printing ink formulation or paint system.

37. Use of the non-aqueous printing ink compositions or paint systems according to claim 35 in printing and painting procedures.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 03/04259

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B69/02 C09B67/22 C09B67/08 C09D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198111 Derwent Publications Ltd., London, GB; Class A89, AN 1981-18521D XP002216318 & JP 56 005552 A (TOYO INK MFG CO), 21 January 1981 (1981-01-21) abstract	1
A	WO 97 35927 A (BASF AG ;PAULUS RUDOLF (DE); DIX JOHANNES PETER (DE); HERRMANN MAN) 2 October 1997 (1997-10-02) example 1 --- -/-	1-28

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/04259

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI  Section Ch, Week 197926  Derwent Publications Ltd., London, GB;  Class D21, AN 1979-48186B  XP002216319  &amp; JP 54 063132 A (SHISEIDO CO LTD),  21 May 1979 (1979-05-21)  abstract</p>	1
A	<p>EP 0 517 513 A (CIBA GEIGY AG)  9 December 1992 (1992-12-09)  abstract; example 1</p>	1-28, 35-37
A	<p>DE 195 47 800 A (CIBA GEIGY AG)  27 June 1996 (1996-06-27)  example 11</p>	1-28, 35-37
A	<p>DE 20 12 152 A (FARBWERKE HOECHST AG)  23 September 1971 (1971-09-23)  page 5, paragraph 2 - paragraph 3  page 1, paragraph 2 - page 2, paragraph 2;  examples</p>	1-3, 35-37
A	<p>WO 99 61534 A (SUN CHEMICAL CORP ; ORTALANO  DARREN MARK (US); VISSING CHRISTOPHER)  2 December 1999 (1999-12-02)  page 6, line 8 - line 10; examples</p>	1-28, 35-37
A	<p>GB 1 356 253 A (CIBA GEIGY UK LTD)  12 June 1974 (1974-06-12)  cited in the application  page 5, line 22 - page 9, line 29</p>	1-28, 35-37
A	<p>EP 0 076 024 A (ICI PLC)  6 April 1983 (1983-04-06)  abstract; examples  &amp; US 4 461 647 A 24 July 1984 (1984-07-24)  cited in the application</p>	1,2
A	<p>EP 0 648 816 A (CIBA GEIGY AG)  19 April 1995 (1995-04-19)  examples</p>	1
A	<p>DE 21 35 468 A (CIBA-GEIGY)  24 February 1972 (1972-02-24)  examples</p>	1-28, 35-37
A	<p>WO 01 10963 A (CABOT CORP)  15 February 2001 (2001-02-15)  abstract</p>	1-28, 35-37

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/04259

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 56005552	A	21-01-1981	JP 1390847 C JP 61061380 B	23-07-1987 25-12-1986
WO 9735927	A	02-10-1997	CN 1214715 A WO 9735927 A1 EP 0889934 A1 KR 2000004920 A US 6080209 A	21-04-1999 02-10-1997 13-01-1999 25-01-2000 27-06-2000
JP 54063132	A	21-05-1979	JP 1390642 C JP 61049349 B	23-07-1987 29-10-1986
EP 0517513	A	09-12-1992	DE 69213830 D1 DE 69213830 T2 DK 517513 T3 EP 0517513 A2 ES 2092041 T3 JP 6088037 A KR 218592 B1 US 5306342 A	24-10-1996 13-03-1997 07-10-1996 09-12-1992 16-11-1996 29-03-1994 01-09-1999 26-04-1994
DE 19547800	A	27-06-1996	DE 19547800 A1	27-06-1996
DE 2012152	A	23-09-1971	DE 2012152 A1 CH 555880 A DK 133823 B FR 2084544 A5 GB 1339068 A JP 55049087 B US 3759731 A	23-09-1971 15-11-1974 26-07-1976 17-12-1971 28-11-1973 10-12-1980 18-09-1973
WO 9961534	A	02-12-1999	CA 2320061 A1 EP 1047739 A1 WO 9961534 A1	02-12-1999 02-11-2000 02-12-1999
GB 1356253	A	12-06-1974	AT 312123 B CA 961607 A1 CH 579623 A5 DE 2122521 A1 DK 151971 B ES 390896 A1 FR 2091301 A5 JP 57037623 B MX 147807 A NL 7106167 A ,B US 3776749 A ZA 7102923 A US 3775148 A	27-12-1973 28-01-1975 15-09-1976 02-12-1971 18-01-1988 01-04-1974 14-01-1972 11-08-1982 13-01-1983 09-11-1971 04-12-1973 26-01-1972 27-11-1973
EP 0076024	A	06-04-1983	AT 15681 T AU 554794 B2 AU 8669982 A CA 1190356 A1 DE 3266393 D1 DK 358582 A ,B, EP 0076024 A1 GB 2108143 A ,B JP 1782973 C	15-10-1985 04-09-1986 17-02-1983 16-07-1985 24-10-1985 12-02-1983 06-04-1983 11-05-1983 31-08-1993

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/04259

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0076024	A		JP 4072865 B	19-11-1992
			JP 58040361 A	09-03-1983
			NO 822716 A ,B,	14-02-1983
			NZ 201300 A	13-12-1985
			US 4461647 A	24-07-1984
			ZA 8205226 A	25-05-1983
EP 0648816	A	19-04-1995	DE 59409101 D1	02-03-2000
			EP 0648816 A1	19-04-1995
			ES 2144503 T3	16-06-2000
DE 2135468	A	24-02-1972	GB 1356254 A	12-06-1974
			BE 770037 A1	17-01-1972
			CA 962006 A1	04-02-1975
			CH 564067 A5	15-07-1975
			DE 2135468 A1	24-02-1972
			FR 2101733 A5	31-03-1972
			NL 7109790 A	18-01-1972
			US 3759733 A	18-09-1973
WO 0110963	A	15-02-2001	AU 6394600 A	05-03-2001
			EP 1218457 A1	03-07-2002
			JP 2003506554 T	18-02-2003
			WO 0110963 A1	15-02-2001